Novel Infrared Vibron Absorption of Solid Hydrogen at Megabar Pressures

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(Received 16 February 1993)

We report new phenomena associated with the infrared-active vibrons in hydrogen at megabar pressures. We find a striking 3 order of magnitude increase in vibron absorbance at the 150 GPa phase transition at 85 K. A discontinuity in the frequency of the infrared vibron is observed which is identical to that measured by Raman spectroscopy at the same temperature. The results indicate there is a significant change in electronic properties at the transition. In addition, the infrared measurements provide evidence for a phase transition at 110 GPa at low temperature.

PACS numbers: 64.70.Kb, 62.50.+p, 78.30.−j

With recent advances in experimental and theoretical capabilities, the behavior of solid hydrogen at ultrahigh pressures has become a subject of intense study. This system has attracted considerable attention because of its possibly highly unusual dynamical and electronic properties in its high density states. At low pressure hydrogen forms a molecular crystal with weak intermolecular interactions, which increase with increasing pressures. A major phase transition in hydrogen was discovered at approximately 150 GPa at 77 K by Raman scattering [1]. The transition is characterized by a discontinuous drop in frequency (~ 100 cm^{-1} at 77 K) of the Raman-active vibron, confirmed in several subsequent spectroscopic studies [2-4]. Of particular note is the fact that the magnitude of the vibron discontinuity diminishes as temperature is increased from 77 K, and the discontinuity disappears altogether at a critical point near 140 K [4]. Above this temperature the Raman vibron frequency decreases continuously with increasing pressures. On the other hand, no significant changes in optical properties in the visible range occur across the transition [5-7]. Despite the growing number of experimental [1-10] and theoretical studies [11-13], the nature of the transition has not yet been determined unequivocally. More recently, there has been new experimental and theoretical evidence for unusual behavior in the dense solid. New phenomena have been observed in the low-frequency Raman spectra of samples in the high-pressure phase [10]. In addition, it has been suggested that new types of pairing interactions and localization phenomena may occur in the high-pressure phase [12,13].

The recent development of synchrotron infrared (ir) spectroscopy at ultrahigh pressures [14] provides the opportunity for a new set of constraints on the nature of the solid at high pressure, including detailed examination of the 150 GPa transition. The $Q_1(J)$ intramolecular stretching mode (vibron) of hydrogen in the frequency range 4000–4600 cm^{-1} observed in the ir is complementary to the study of the Raman vibron which has been the only criterion for the 150 GPa transition in hydrogen. It is crucial to determine whether the discontinuity, the phase boundary, and the critical point also exist for the ir vibron. The existence of these properties would indicate that the transition is intrinsic to the intramolecular vibration and represents the actual softening of the zone-center vibron. The absence of a vibron discontinuity in the infrared, for example, could indicate that the transition is merely associated with a change in vibron band structure.

We report here several unexpected phenomena associated with the infrared-active vibron encountered during continued characterization of hydrogen at megabar pressures by infrared spectroscopy. We observe a new absorption line in the vibron frequency range appearing at 110 GPa, followed by a discontinuity in the infrared vibron at 150 GPa. Further, there is a striking 3 order of magnitude increase in absorptivity at this pressure. Together with observation of the infrared vibron discontinuity, the results indicate that there is a large electronic change at the 150 GPa transition.

The measurements were performed on a new synchrotron infrared beam line (U2B) dedicated to mid-ir ultrahigh pressure spectroscopy at the National Synchrotron Light Source, Brookhaven National Laboratory. Hydrogen samples were loaded in modified megabar (Mao-Bell) diamond cells. The cell was placed in a specially designed liquid-nitrogen Dewar in which both ir absorption and Raman spectra can be measured on the same sample at high pressures and low temperatures. Infrared spectra were measured with a Nicolet 740 Fourier transform spectrometer. Raman spectra were measured using an argon-ion or krypton-ion laser for excitation and a 320 mm spectrograph with a charge coupled device detector. Only pure hydrogen (free of any additional materials such as ruby grains for pressure measurements) was placed in the sample chamber. The previously measured pressure dependence of the Raman vibron of hydrogen was used to determine pressure [15]. This procedure also provides a direct comparison of the ir and Raman vibrons, which was one of the primary goals of this study.

Hydrogen samples, with the approximate size of 20 μm diameter and 2–3 μm thickness above 100 GPa, were studied at 85 K up to 210 GPa. Representative absorp-

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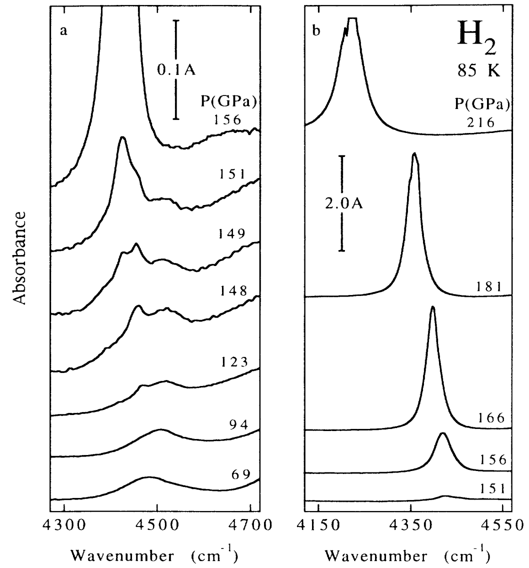

FIG. 1. Absorption spectra of hydrogen at 85 K in the frequency range of the $Q_1(J)$ ir vibron. (a) Low-pressure phases. (b) High-pressure phase to 216 GPa. The absorption measurements cover a spectral range of 3000–6500 cm^{-1}. Above 4800 cm^{-1} additional weak bands, which can be assigned to combinations of the vibron and rotational excitations $[Q_1(J)+S_0(J)]$ or lattice modes $[Q_R(J)]$, were observed [28].

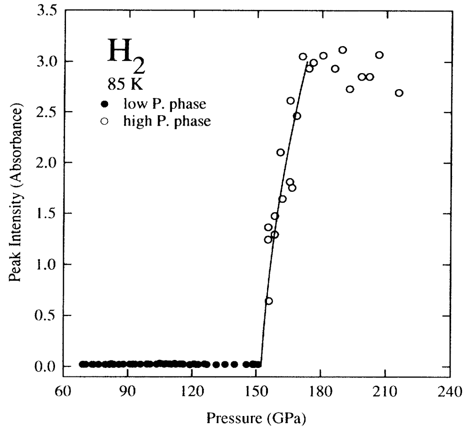

FIG. 2. Peak absorbance of the vibron as a function of pressure at 85 K. Full circles, low-pressure phase; open circles, high-pressure phase. The line is a guide to the eye.

tion spectra at 85 K are presented in Fig. 1. At low pressure one band is observed between 4000 and 4600 cm^{-1}, which can be assigned to the $Q_1(J)$ ir vibron. With increasing pressures a sharp peak (FWHM$=$20 cm^{-1}) appears 45 cm^{-1} below the vibron band [Fig. 1(a)]. The intensity of this new peak increases with pressure while that of the vibron band remains essentially unchanged. Measurements at 295 [14] and 140 K [16] show no evidence for the peak. At 150 GPa a third line appears 85 cm^{-1} below the vibron band while the higher frequency peaks begin to disappear. The intensity of the third line increases dramatically with further increase in pressure [Fig. 1(b)]. Measurements of Raman spectra show that this change occurs simultaneously with the appearance of the Raman vibron of the high-pressure phase. We therefore identify this line with an ir-active vibron of the high-pressure phase. The transition was reversed by decreasing the pressure, and no hysteresis was observed, consistent with previous Raman measurements [1,2,4]. The experiment was repeated 4 times with new sets of diamond anvils and new hydrogen samples to confirm all observed phenomena.

The measured peak absorbance of the ir vibrons is shown as a function of pressure in Fig. 2. For the low-pressure phase, the vibron absorbance of a 3 μm thick hydrogen sample is 0.02, which corresponds to an absorption coefficient of 66 cm^{-1}, and the FWHM is 100 cm^{-1}. After the transition, the vibron absorbance rapidly increases several orders of magnitude saturating at 3.0 at 175 GPa. An absorbance of 3.0, which corresponds to an absorption coefficient of 10^4 cm^{-1} for a 3 μm thick sample, means a transmission signal of 10^{-3} of the incident beam, which is our limit for accurate intensity measurements. It is therefore likely that the absorption may continue to rise even further with increasing pressure above 175 GPa. This can be studied by using even thinner samples. The FWHM of the high-pressure ir vibron narrows to 35 cm^{-1}, a change opposite to the behavior of the Raman vibron, which in our measurements broadens from 22 cm^{-1} before the transition to 45 cm^{-1} after the transition. A rapid (but smaller) increase in absorbance above 150 GPa is also observed at 140 K, reaching a value of 1.2 at $\sim$190 GPa. A much smaller increase is observed at 295 K [14,17].

The measured frequencies for the 85 K isotherm of ir and Raman modes of the hydrogen $Q_1(J)$ vibron are plotted as a function of pressure in Fig. 3. The 295 K isotherm is also plotted for comparison. Because of the strong blue absorption and luminescence of the diamond anvils at ultrahigh pressures [18,19], the Raman signal of hydrogen becomes very weak and was not measured with sufficient accuracy above 181 GPa; thus we estimated the pressure for the ir spectra by extrapolation of the lower-pressure data [20]. At 85 K, the ir vibron of hydrogen increases with pressure up to 150 GPa, drops 85 cm^{-1} at the transition, and decreases with pressure at an increasing rate above the transition. The transition pressures are identical in ir and Raman measurements. The frequency discontinuities in the ir and Raman vibrons are identical in sign and magnitude too. At 140 K, close to the critical temperature found in Raman experiments [4], and at 295 K the frequency of the ir vibron decreases continuously above 140 GPa. No discontinuities have been observed up to $\sim$190 and 180 GPa, respectively. The above re-

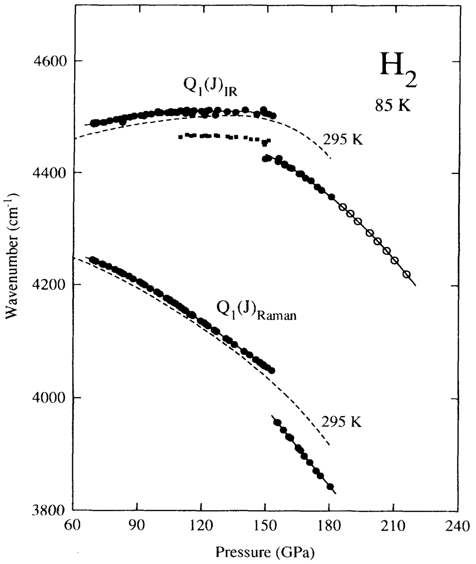

FIG. 3. $Q_1(J)$ ir and Raman vibron frequencies of hydrogen as a function of pressure at 85 K. Open circles, pressures estimated on the basis of extrapolation of lower-pressure data; squares, sharp peak appearing at 110 GPa; and dashed lines, ir and Raman frequencies at 295 K [14].

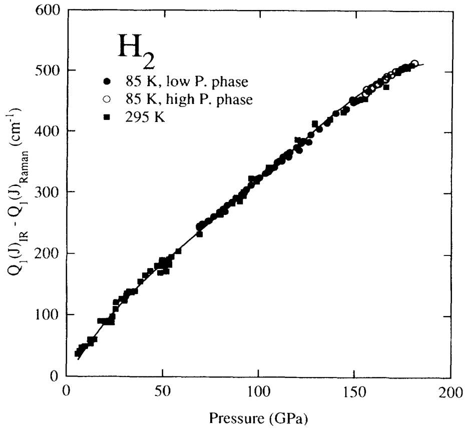

FIG. 4. Difference between the ir and Raman vibron frequencies as a function of pressure; full circles, 85 K, low-pressure phase; open circles, 85 K, high-pressure phase; and squares, 295 K [14].

sults show that phase boundary and critical behavior observed in ir absorption measurements correspond exactly with those determined by Raman spectroscopy.

The difference between the ir and Raman vibrons, $Q_1(J)_{\mathrm{ir}} - Q_1(J)_{\mathrm{Raman}}$, is a measure of intermolecular vibrational coupling [14,21], and is plotted in Fig. 4. The data at 85 K completely overlap those at 295 K [14] and are continuous across the phase transition within the experimental error. Thus, a discontinuous change occurs in the intramolecular vibration at the 150 GPa transition whereas the change in intermolecular vibrational coupling is insignificant. Furthermore, the magnitude of the intermolecular coupling increases rapidly and with the same rate before and after the transition.

In addition to the change at 150 GPa, evidence for a new transition is observed at 110 GPa as indicated by the new sharp peak which appears 45 cm^{-1} below the principal vibron [Figs. 1(a) and 3]. The new peak was not observed at 140 and 295 K, nor does it appear in the low-temperature Raman spectra. This new peak may be related to a molecular ordering transition. The splitting of the vibron may indicate that the ordered state has a lower symmetry than hcp. Proposed ordered structures include the flat or tilted herringbone derivative of fully disordered hcp [22]. Evidence for ordering on the basis of broadening and loss of the low frequency rotational Raman bands was reported for pure parahydrogen at 8 K at comparable pressures [9]. On the other hand, measurements carried out at 77 K show that for normal hydrogen these bands can be measured through this pressure range [8]. Also, no significant change of the $Q_1(J)+S_0(J)$ vibron roton combination bands is observed in the absorption spectra at the appearance of the peak.

We now return to the striking enhancement of absorption of the vibron at the 150 GPa transition. The intensity of ir absorption A is a measure of the change of electric dipole moment μ between the two states i and j, $A \propto |\langle i|\mu|j\rangle|^2$. Excitation of the intramolecular stretching mode in the isolated molecule is forbidden. Although in the solid phase, electric dipole moments are induced by intermolecular interactions [21], the induced moments and the resultant ir absorption are weak. The absorption coefficient of the $Q_1(J)$ transition of the solid increases with the square of density, but its maximum is still less than 50 cm^{-1} at 50 GPa [23] (relative density $\rho/\rho_0=6$) [24]. This indicates that despite the monotonic increase in intermolecular vibrational coupling [14], the basic electronic properties change only moderately with pressure in this range (including at the 110 GPa phase transition). We suggest that the dramatic increase in absorption indicates that the vibronic (electron-vibron) coupling has increased in the high-pressure phase above 150 GPa. This implies an interaction between an electronic state (or states) and the intramolecular stretching mode [25]. Although the specific form of the coupling has not been determined, this proposal is consistent with the enhancement of the pure vibron $Q_1(J)$ relative to the combination bands $[Q_1(J)+S_1(J)$ and $Q_R(J)]$.

We conclude that the transition is best viewed as one in which electrons are partially removed from the molecular bond, thus causing the discontinuous drop of ir and Raman vibron frequencies and weakening the bond. Such redistribution of charge, associated either with electrons moving into the conduction band [26] or the formation of an electron-hole pair [4,13], would create a significant transition moment in the high-pressure phase, as observed. The intensity change is also likely coupled with structural distortions [22]. Notably, some parallels may be found in the infrared response and vibronic coupling documented for organic conductors and charge-transfer compounds at zero pressure. In these systems, intramolecular modes couple with low-lying charge-transfer or Drude-type transitions to give large enhancements in the fundamental transitions in infrared absorption [27]. The visible and near-infrared transparency of the high-pressure phase indicates that if it is metallic, its electron carrier density is low [5-7,17]. An insulating ground state could arise if the electrons have limited path length due to disorder-induced localization or the formation of excitonic (or possibly other novel) states [4,10,12,13]. The extent of ionization and localization, the nature of the electron-vibron coupling, and a quantitative theory of extraordinary infrared response documented here are thus of considerable interest for future experimental and theoretical study of the dense molecular solid.

We thank J. H. Eggert, Z. Soos, and N. W. Ashcroft for useful discussions, and J. F. Shu for help with the experiments. This work was supported by NSF (DMR-8912226, EAR-8920239), NASA (NAGW1722), and DOE (DE-AC-2-76CH00016).

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